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TI **Polyoxymethylene** copolymer compositions with high tensile strength and impact and bending resistance

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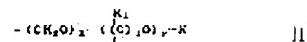
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(21)Application number : **11-239454**(71)Applicant : **ASAHI CHEM IND CO LTD**(22)Date of filing : **26.08.1999**(72)Inventor : **NAKAMURA HIDEKI**
TOKI MAKOTO**(54) POLYOXYMETHYLENE COPOLYMER COMPOSITION****(57)Abstract:**

PROBLEM TO BE SOLVED: To obtain the subject composition satisfying tensile elongation, repeated impact and hinge characteristics at a low temperature by bringing the composition to contain a specific copolymer and a specific polymer.

SOLUTION: This polyoxymethylene copolymer composition is brought to contain 100 pts.wt. of (A) a polyoxymethylene copolymer containing a hydroxyalkyl(HA) group on the molecular end and $\geq 5 \times 10^{-5}$ mole terminal HA group concentration per 1 mol of the oxymethylene unit and 1-100 pts.wt. of a modified α -olefin copolymer. As the ingredient A, a copolymer and the like having 10000-500000 number average molecular weight and expressed by formula I [the part except A is a hydrogen-added liquid polybutadiene residue and the like hydroxyalkylated on both ends and having 500-10000 number average molecular weight, m=2-98 mole %, n=2-98 mole %, m+n=100 mole % and m is random or block against n; k=2-6; R is H or the like; A is a copolymer residue having 5000-250000 number average molecular weight and expressed by formula II (R1 is R; j is k; x=95-99.9 %, y=5-0.1 %, x+y=100 %, y is random against x)] are cited.



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CLAIMS

[Claim(s)]

[Claim 1] (A) The polyoxymethylene copolymer constituent characterized by a molecule end carrying out 1-100 weight section content of the (B) denaturation alpha olefin system polymer to the polyoxymethylene copolymer 100 weight section which the hydroxylalkyl machine end concentration has more than 5×10^{-5} mol per one mol of oxy-methylene units including a hydroxylalkyl machine.

[Claim 2] The polyoxymethylene copolymer constituent according to claim 1 characterized by being the alpha olefin system polymer which the aforementioned denaturation alpha olefin system polymer denaturalized by the unsaturation dicarboxylic acid or its acid anhydride.

[Claim 3] The polyoxymethylene copolymer constituent according to claim 1 or 2 characterized by manufacturing the aforementioned denaturation alpha olefin system polymer using a single site catalyst.

[Claim 4] A polyoxymethylene copolymer constituent given in any 1 term of the claims 1-3 characterized by the aforementioned denaturation alpha olefin system polymers being one or more sorts of ethylene and the alpha olefin of carbon numbers 3-20 of copolymers.

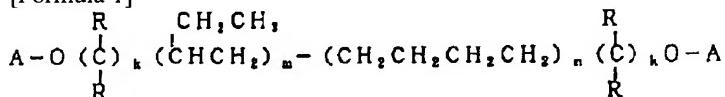
[Claim 5] A polyoxymethylene copolymer constituent given in any 1 term of the claims 1-4 which blend the JII fatty-acid calcium 0.01 which consists of two or more sorts of fatty acids which are carbon numbers 10-36 - the 0.2 weight sections to the total 100 weight section of the (A) and the (B) component of a claim 1, and are characterized by the bird clapper.

[Claim 6] A polyoxymethylene copolymer constituent given in any 1 term of the claims 1-5 to which the polyoxymethylene copolymer (aforementioned [A]) is characterized by being the polyoxymethylene copolymer which has 10xten - five or more mols per one mol of oxy-methylene units of hydroxylalkyl machine end concentration by using together and using a formal if needed further by making water or ten or less-carbon number fatty alcohol into a chain transfer agent.

[Claim 7] A polyoxymethylene copolymer constituent given in any 1 term of the claims 1-5 characterized by being the polyoxymethylene block copolymer obtained by copolymerizing an annular acetal, and cyclic ether and/or an annular formal, using the polymer whose polyoxymethylene copolymer (aforementioned [A]) is the molecular weight 500-10,000 which has at least one or more hydroxyl groups as a chain transfer agent.

[Claim 8] claim 1- characterized by the polyoxymethylene copolymer (aforementioned [A]) being a polyoxymethylene block copolymer of number average molecular weight 10,000-500,000 expressed with the following formula (1) -- a polyoxymethylene copolymer constituent given in 5 or 7 any 1 terms

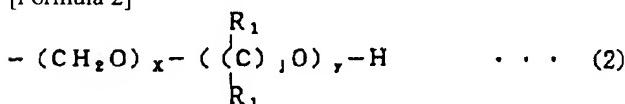
[Formula 1]



... (1)

(The hydrogenation liquid polybutadiene residue which exists with a block and by which was been $m=2-98$ -mol % and $m+n=100$ -mol % among the formula except A (henceforth B blocks), and m was hydroxylalkyl-ized to n in random or the both ends which is number average molecular weight 500-10,000.) [% and $n=2-98$ mol] However, you may have B blocks of iodine number 20 g-I2 / unsaturated bonds 100g or less. It is the integer chosen from $k=2-6$, and even if two k is respectively the same, it may differ. R is chosen from hydrogen, an alkyl group, a substitution alkyl group, an aryl group, and a substitution aryl group, and even if respectively the same, it may differ. A is a polyoxymethylene copolymer residue expressed with the following formula (2).

[Formula 2]



(R1 is chosen from hydrogen, an alkyl group, a substitution alkyl group, an aryl group, and a substitution aryl group, and even if respectively the same, it may differ.) j is an integer chosen from 2-6. y exists at random to $x \ x=95-99.9$ -mol % and $x+y=100$ -mol%. The inside of the aforementioned formula (1), two number average molecular weight 5,000-250,000 of an A-block

average [% and y= 5-0.1 mol]

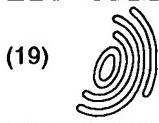
[Claim 9] A polyoxymethylene copolymer constituent given in any 1 term of the claims 1-8 to which the polyoxymethylene copolymer (aforementioned [A]) is thermally characterized by processing an unstable end and making it stabilize at least using the 4th class ammonium compound of a kind of expressed with the following formula (3).

[Formula 3]



(R1, R2, R3, and R4 among a formula) It becomes independent respectively. The unsubstituted alkyl group of carbon numbers 1-30 Or substitution alkyl group; The aryl group of aralkyl machine; by which the unsubstituted alkyl group or substitution alkyl group of carbon numbers 1-30 was replaced by the aryl group of at least one carbon numbers 6-20, or carbon numbers 6-20 The aryl group of carbon numbers 6-20; The unsubstituted alkyl group of at least one carbon numbers 1-30 Or the alkyl aryl machine replaced by the substitution alkyl group is expressed, and an unsubstituted alkyl group or a substitution alkyl group is the shape of a straight chain, a letter of branching, or annular. As for the above-mentioned unsubstituted alkyl group, an aryl group, an aralkyl machine, and an alkyl aryl machine, a hydrogen atom may be replaced by the halogen. n expresses the integer of 1-3. X expresses the acid residue of a hydroxyl group or the carboxylic acid of carbon numbers 1-20, a hydro acid, an oxo acid inorganic thio acid, or the organic thio acid of carbon numbers 1-20.

[Translation done.]



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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the new polyoxymethylene copolymer constituent which was excellent in flexibility, tension ductility, and repeat shock nature, and was excellent in the hinge property in low temperature. Conventionally, a polyoxymethylene resin begins various kinds of mechanism elements as engineering plastics excellent in the mechanical property and the heat-resistant property, and is widely used for OA equipment etc. However, if a polyoxymethylene resin has a low repeat impact strength and the residual stress and the small blemish at the time of molding exist, it has the fault of being easy to destroy. Therefore, the present condition is not adopted as the use which needs repeat shock nature and flexibility, and to improve the repeat shock nature and flexibility of a polyoxymethylene resin was desired strongly.

[0002]

[Description of the Prior Art] The method (JP,43-22669,B, JP,45-26231,B, JP,45-18023,B) of adding alpha olefin polymers of polar-group content, such as the method (JP,41-2730,B, JP,42-19498,B, JP,43-20376,B, JP,50-103556,B) of adding an olefin polymer and an alpha olefin polymer, in order to improve the shock resistance of a polyoxymethylene resin and flexibility, an ethylene vinyl acetate copolymer, and an ethylene acrylic-acid copolymer, etc. is learned. However, since the polyoxymethylene resin which are the amorphous polymer and crystalline polymers which are used in these methods, such as an olefin polymer and an alpha olefin polymer, originally lacks in compatibility, melting and the constituent obtained even if kneaded tend to exfoliate such mixture in layers, and *** does not have [sufficient mechanical strength not being obtained upwards and becoming poor / the appearance of a cast /, and] **.

[0003] Moreover, to JP,3-12583,B, a denaturation alpha olefin system polymer is kneaded to the usual polyoxymethylene resin, and Izod impactive strength is improved. However, although the example of comparison describes the back, it turns out neither tension ductility nor a repeat shock, and that the hinge property in low temperature is improved further. Furthermore, to JP,3-30628,B, the ethylene copolymer was blended with the polyoxymethylene block copolymer which consists of a polyoxymethylene portion and an elastomer portion, and a shock-proof improvement is tried. However, about the molecule end in the polyoxymethylene block copolymer in JP,3-30628,B, 21-23 lines of P.10 have "addition is presented after changing a polymer end into a stable basis after polymerization reaction", and a publication, and an example 3 has further description which has acetylated the end of a polyoxymethylene block copolymer.

[0004] Therefore, the molecule end of the polyoxymethylene block copolymer currently indicated by JP,3-30628,B is not a hydroxyalkyl machine end as used in the field of this invention, does not differ in thought at all with this invention, and does not suggest this invention. Furthermore, about an effect, although Izod impactive strength is improved, it turns out too neither tension ductility nor a repeat shock, and that the hinge property in low temperature is improved further.

[0005]

[Problem(s) to be Solved by the Invention] this invention is the basis of such a situation and is made for the purpose of offering especially tension ductility, a repeat shock, and the polyoxymethylene copolymer-resin constituent with which it is simultaneously satisfied of the hinge property in low temperature further.

[0006]

[Means for Solving the Problem] As a result of inquiring wholeheartedly that this invention persons should attain the aforementioned purpose, it is that in which (A) molecule end contains a hydroxyalkyl machine. And the polyoxymethylene copolymer 100 weight section which 5xten - five or more mols per one mol of oxy-methylene units of the hydroxyalkyl machine end concentration have is received. (B) While the repeat impact strength was remarkably improved by blending the 1 - 100 weight section in the denaturation alpha olefin system polymer, it found out that the polyoxymethylene resin constituent excellent in tension ductility and the hinge property in low temperature was obtained, and resulted in this invention.

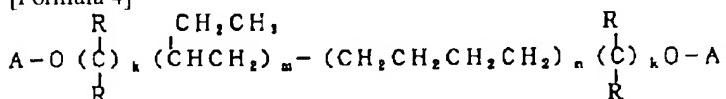
[0007] It explains in detail below. The polyoxymethylene copolymer used as a (A) component in this invention It is what is contained. annular oligomer, such as formaldehyde, a trioxane which is the trimer, or tetramer tetrapod oxane, -- a polymerization -- carrying out -- an oxy-methylene unit -- more than 80 mol % -- as a component not more than 20 mol % An ethyleneoxide, propylene oxide, 1, 3-dioxolane, Cyclic ether, such as a formal of a glycol, and a formal of diethylene glycol, And/or, it is the polymer which has a hydroxyl, a carboxyl group, the amino group, an ester machine, and an alkoxy group, and they are copolymerization and/or the polyoxymethylene copolymer which was made to carry out block copolymerization and was obtained about them.

[0008] Furthermore, the hydroxyalkyl machine end concentration says [the molecule end in the above-mentioned polyoxymethylene copolymer] more preferably 5xten - five or more mols per one mol of oxy-methylene units, and the polyoxymethylene copolymer which it has 30xten - five or more mols preferably especially 10xten - five or more mols especially including a hydroxyalkyl machine. Although there are various methods in order to adjust the hydroxyalkyl machine end concentration in the above-mentioned polyoxymethylene copolymer when it states in more detail, the chain transfer of water, alcohol (for example, methanol), the acid (for example, formic acid), etc. may be carried out, for example, and the chain transfer of the polymer containing a hydroxyl group may be carried out. Moreover, you may add a formal called a methylal simultaneously if needed.

[0009] It is the polyoxymethylene block copolymer to which the chain transfer of the polymer which is the molecular weight 500-10,000 which contains a hydroxyl group as a desirable thing was carried out especially, for example, is a polyoxymethylene block copolymer using the polyethylene of a piece end or a both-ends hydroxyl group, the hydrogenation polybutadiene, the hydrogenation polyisoprene, etc. It is the polyoxymethylene block copolymer which is the number average molecular weight 10,000-500,000 expressed with the following formula (1) still more preferably.

[0010]

[Formula 4]

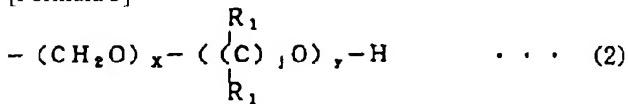


... (1)

(The hydrogenation liquid polybutadiene residue which exists with a block and by which was been $m=2.98\text{-mol \%}$ and $m+n=100\text{-mol \%}$ among the formula except A (henceforth B blocks), and m was hydroxyalkyl-ized to n in random or the both ends which is number average molecular weight 500-10,000.) [% and $n=2.98\text{ mol}$] However, you may have B blocks of iodine number 20 g-I2 / unsaturated bonds 100g or less. It is the integer chosen from $k=2-6$, and even if two k is respectively the same, it may differ. R is chosen from hydrogen, an alkyl group, a substitution alkyl group, an aryl group, and a substitution aryl group, and even if respectively the same, it may differ. A is a polyoxymethylene copolymer residue expressed with the following formula (2).

[0011]

[Formula 5]



(R1 is chosen from hydrogen, an alkyl group, a substitution alkyl group, an aryl group, and a substitution aryl group, and even if respectively the same, it may differ.) j is an integer chosen from 2-6. y exists at random to $x=95.99.9\text{-mol \%}$ and $x+y=100\text{-mol \%}$. The inside of the aforementioned formula (1), two number average molecular weight 5,000-250,000 of an A-block average [% and $y=5.0.1\text{ mol}$]

The compatibility to the polyoxymethylene copolymer of the denaturation alpha olefin system polymer whose hydroxyalkyl machine end concentration in a polyoxymethylene copolymer is the (B) component in less than 5xten - five mols per one mol of oxy-methylene units falls, and it becomes a maldistribution. A repeat impact strength and a low-temperature hinge property get worse at the same time the fall of tension ductility is seen for the reason.

[0012] As a polymerization catalyst, cation activity catalysts, such as a Lewis acid, a proton acid and its ester, or an anhydride, are desirable. As a Lewis acid, the halogenide of a boric acid, tin, titanium, Lynn, an arsenic, and antimony is mentioned, and a boron trifluoride, a tin tetrachloride, a titanium tetrachloride, phosphorus pentafluoride, a phosphorus pentachloride, 5 antimony fluoride and its complex compound, or a salt is specifically mentioned, for example. Moreover, as an example of a proton acid, its ester, or an anhydride, a par crawl acid, a trifluoromethane sulfonic acid, the 3rd [-] class butyl ester of a par crawl acid, acetyl par clo RATO, trimethyl oxonium hexafluorophosphate, etc. are mentioned. Especially the coordination complex compound of the organic compound and boron trifluoride containing boron-trifluoride; boron-trifluoride hydrate; and an oxygen atom, or a sulfur atom is desirable. specifically Boron-trifluoride diethylether and a boron-trifluoride G n-butyl ether can be mentioned as a suitable example. The amount of these polymerization catalysts used has 1xten - six mols - desirable 1xten - three mols to one mol of total quantities of a trioxane, cyclic ether, and/or an annular formal, and 5xten - six mols - its 1xten - four mols are still more desirable.

[0013] although there is especially no limit as a polymerization method -- a bulk polymerization -- it can mention -- this bulk polymerization -- a batch type and continuous system -- you may be any As for this bulk polymerization, it is common to obtain the polymer of a solid-state massive with advance of a polymerization using the monomer in a melting state. Deactivation of the polymerization catalyst in the polyoxymethylene copolymer by which the polymerization was carried out supplies the polyoxymethylene copolymer obtained by the aforementioned polymerization reaction in the solution of catalyst neutralization quenchers, such as a hydroxide of amines, such as ammonia, a triethylamine, and tree n butylamine, alkali metal, or alkaline earth metal, an inorganic-acid salt, and organic acid chloride, which contains a kind at least, or an organic-solvent solution, and is performed by generally stirring by the slurry regime for several minutes to several hours. The slurry after catalyst neutralization deactivation is dried by filtration and washing after an unreacted monomer, a catalyst neutralization quencher, and a catalyst

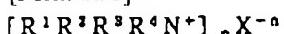
neutralization deactivation salt are removed.

[0014] Moreover, the method of contacting a kind and a polyoxymethylene copolymer with a mixer at least, and making a catalyst deactivate of the method of contacting a steam and polyoxymethylene copolymers, such as ammonia and a triethylamine, and making a polymerization catalyst deactivating, hindered amine, triphenyl phosphine, calcium hydroxides, etc. can also be used.

[0015] Next, the end stabilizing treatment of the polyoxymethylene copolymer after polymerization-catalyst deactivation is described. Under existence of the alkali which can decompose unstable ends, such as a hydroxide, an inorganic weak-acid salt, an organic weak-acid salt, etc. of the alkali metal represented by fatty amines, such as ammonia, and a triethylamine, tributylamine, and the calcium hydroxide or alkaline earth metal, for example, using a monopodium screw-type extruder with a vent, a biaxial with a vent] screw-type extruder, etc. as the decomposition removal method of an unstable end, a polyoxymethylene copolymer can be fused and decomposition removal of the unstable end can be carried out. Especially, especially a desirable thing is the method of processing an unstable end thermally using a kind of 4th class-at least ammonium compound expressed with the following formula (3), and the unstable end does not almost remain into the polyoxymethylene copolymer stabilized by the above-mentioned method.

[0016]

[Formula 6]



(R1, R2, R3, and R4 among a formula) It becomes independent respectively. The unsubstituted alkyl group of carbon numbers 1-30 Or substitution alkyl group; The aryl group of aralkyl machine; by which the unsubstituted alkyl group or substitution alkyl group of carbon numbers 1-30 was replaced by the aryl group of at least one carbon numbers 6-20, or carbon numbers 6-20 The aryl group of carbon numbers 6-20; The unsubstituted alkyl group of at least one carbon numbers 1-30 Or the alkyl aryl machine replaced by the substitution alkyl group is expressed, and an unsubstituted alkyl group or a substitution alkyl group is the shape of a straight chain, a letter of branching, or annular. As for the above-mentioned unsubstituted alkyl group, an aryl group, an aralkyl machine, and an alkyl aryl machine, a hydrogen atom may be replaced by the halogen. n expresses the integer of 1-3. X expresses the acid residue of a hydroxyl group or the carboxylic acid of carbon numbers 1-20, a hydro acid, an oxo acid inorganic thio acid, or the organic thio acid of carbon numbers 1-20.

[0017] About the compound of the above-mentioned quarternary ammonium salt Specifically Tetramethylammonium, a tetraethylammonium, Tetrapropylammonium, tetrapod-n-butyl ammonium, cetyl trimethylammonium, Tetradecyl trimethylammonium, 1, 6-hexamethylene screw (trimethylammonium), Deca methylene-screw - (trimethylammonium) and trimethyl-3-chloro-2-hydroxypropyl ammonium, TORIMECHIRU (2-hydroxyethyl) ammonium, triethyl (2-hydroxyethyl) ammonium, TORIPUROPIRU (2-hydroxyethyl) ammonium, tree n-butyl (2-hydroxyethyl) ammonium, Trimethyl benzyl ammonium, triethyl benzyl ammonium, TORIPURO pill benzyl ammonium, tree n-butyl benzyl ammonium, Trimethyl phenyl ammonium, triethyl phenyl ammonium, Trimethyl-2-oxy-ethylammonium, monomethyl trihydroxy ethylammonium, Monoethyl trihydroxy ethylammonium, OKUTADESHIRUTORI (2-hydroxyethyl) ammonium, Hydro-acid salts other than halogenation of a hydroxide; hydrogen azide etc. of tetrakis (hydroxyethyl) ammonium etc.; A sulfuric acid, A nitric acid, phosphoric acid, carbonic acid, a boric acid, a chloric acid, iodic acid, silicic acid, perchloric acid, a chlorous acid, Thio-acid salts [, such as an oxo acid salt; thiosulfuric acid], such as a hypochlorous acid, a chlorosulfuric acid, an amidosulfuric acid, a disulfuric acid, and Tripoli phosphoric acid; Formic acid, Carboxylates, such as an acetic acid, a propionic acid, a butanoic acid, an isobutyric acid, a pentanoic acid, a caproic acid, a caprylic acid, a capric acid, a benzoic acid, and oxalic acid, etc. are mentioned. Especially, the salt of a hydroxide (OH-), a sulfuric acid (HSO4- and SO42-), carbonic acid (HCO3- and CO32-), a boric acid (B(OH)4-), and a carboxylic acid is desirable. Formic acid, an acetic acid, and especially a propionic acid are desirable among carboxylic acids.

[0018] These 4th class ammonium compound may be used independently, and may be used combining two or more sorts. The addition of the 4th class ammonium compound is converted into the amount of the nitrogen of the 4th class ammonium compound origin expressed with the following formula (4) to a polyoxymethylene copolymer, and is the 0.05 - 50 weight ppm.

Px14/Q (4)

(P expresses the concentration (weight ppm) to the polyoxymethylene copolymer of the 4th class ammonium compound among a formula, 14 is the atomic weight of nitrogen and Q expresses the molecular weight of the 4th class ammonium compound.)

[0019] Next, the end group of the polyoxymethylene copolymer chain contained in the polyoxymethylene copolymer in this invention is explained in detail. In this invention, the end groups which two or more polyoxymethylene copolymer chains which constitute a polyoxymethylene copolymer have as a whole are hydroxyalkyl machines, such as alkoxy groups, such as a methoxyl group (-OCH3), and a hydroxyethyl machine (-CH2 CH2 OH), and a formate machine. At least one end alkoxy group is formed of the formal which is the regulator by which a carbon number is added in a polymerization stage. For example, although a methylal [(CH3 O)2 CH2] is generally used as a regulator, as an end group, a methoxyl group is formed in this case. Although especially the carbon number of an end alkoxy group is not limited, from composition and the refining side of the formal which is a regulator, it is common that they are carbon numbers 1-10, and it is desirable that they are carbon numbers 1-3.

[0020] As a regulator in a polymerization stage, in case water, alcohol (for example, methanol), an acid (for example, formic acid), etc. are used, or when the chain transfer of the compound which has a hydroxyl group is carried out to an end and a hydroxyethyl machine and an end hydroxyalkyl machine like a hydroxy butyl use it for it, a hydroxymethyl group (-CH2 OH) generates them first. If the polyoxymethylene copolymer which has a hydroxymethyl group at this end is given to heat-treatment under existence of after treatment, for example, alkaline matter solution like triethylamine solution, the unstable portion

containing a hydroxymethyl group will decompose. If this decomposition advances the inside of a principal chain including an oxy-methylene unit and an oxy-alkylene unit [inside] and reaches the portion of an oxy-alkylene unit, the oxy-alkylene unit of the portion will change to stable ends, such as a hydroxyethyl machine and a hydroxy butyl. Although especially the carbon number of a hydroxalkyl machine is not limited, and it is generally at least two pieces, it is desirable from composition and the refining side of cyclic ether and an annular formal that it is 2-10.

[0021] Next, the denaturation alpha olefin system polymer used as a (B) component is explained. The 0.01-10 weight section graft copolymerization of a unsaturated carboxylic acid or its acid-anhydride component unit is carried out to the alpha olefin system polymer 100 weight section whose denaturation alpha olefin system polymer is a basis. As the unsaturated carboxylic acid or its acid-anhydride component unit of the graft monomer component to constitute An acrylic acid, a methacrylic acid, alpha-ethyl acrylic acid, a maleic acid, boletic acid, An itaconic acid, a citraconic acid, a tetrahydrophthal acid, endo-cis bicyclo [2, 2, 1] HEPUTO 5-EN 2, 3 dicarboxylic acids (NAJITSUKU acid), Unsaturated carboxylic acids, such as MECHIRU endo-cis bicyclo [2, 2, 1] HEPUTO 5-EN 2 and 3 dicarboxylic acids (methyl NAJITSUKU acid), A maleic anhydride, an anhydrous citraconic acid, itaconic acid anhydride, an anhydrous tetrahydrophthal acid, an anhydrous NAJITSUKU acid, an anhydrous methyl NAJITSUKU acid, etc. are illustrated by the anhydride of this unsaturated carboxylic acid, and the concrete target. In these, an unsaturation dicarboxylic acid or its acid anhydride is desirable, and a maleic acid or especially a maleic anhydride is still more desirable. moreover, as an alpha olefin component unit which constitutes this denaturation alpha olefin system polymer Ethylene, a propylene, Butene-1, a pentene -1, 4-methyl pentene -1, a hexene -1, a heptene -1, an octene 1, a nonene -1, decene -1, undecene -1, dodecen -1, tridecenoic -1, tetrapod decene -1, pentadecene-1, hexa decene -1, heptadecene -1, Aliphatic substitution vinyl monomers, such as octadecene -1, nonadecen -1 or ray KOSEN -1, and an isobutylene, Aromatic system vinyl monomers, such as styrene and substitution styrene, vinyl acetate, An acrylic ester, methacrylic-acid ester, a glycidyl acrylic ester, Ester system vinyl monomers, such as glycidyl methacrylic-acid ester and hydroxyethyl methacrylic-acid ester, Dienes, such as nitrogen content vinyl monomers, such as an acrylamide, an allylamine, vinyl-p-aminobenzene, and acrylonitrile, a butadiene, a cyclopentadiene, 1, 4-hexadiene, and an isoprene, etc. can be raised, and it consists of one sort or two above-mentioned sorts or more. As for this alpha olefin system polymer, what was manufactured using the single site catalyst is still more desirable. with a single site catalyst The Patent Publication **** No. 12283 [four to] official report, JP,60-35006,A, JP,60-35007,A, JP,60-35008,A, JP,63-280703,A, Carry out 1-3 molecule content of the cyclopentadienyl or substitution cyclopentadienyl indicated by JP,5-155930,A, JP,3-163088,A, and the U.S. Pat. No. 5272236 specification. It is a catalyst with the uniform property of the active spots, such as a metallocene catalyst and a catalyst by geometric control.

[0022] The contents of desirable cyclopentadienyl or substitution cyclopentadienyl are 1 - dyad. Furthermore, the metal components used more preferably are titanium, a zirconium, silicon, and a hafnium.

[0023] Concretely as a desirable metallocene catalyst Cyclopentadienylzirconium trichloride, pentamethylcyclopentadienyl zirconium trichloride, Screw (cyclopentadienyl) zirconium dichloride, screw (cyclopentadienyl) zirconium monomethyl monochrome chloride, Screw (methylcyclopentadienyl) zirconium dichloride, screw (pentamethylcyclopentadienyl) zirconium dichloride, Screw (ethylcyclopentadienyl) zirconium dichloride, a screw (cyclopentadienyl) zirconium dialkyl, Screw (cyclopentadienyl) zirconium diphenyl, a dimethylsilyl dicyclopentadienyl zirconium dimethyl, Zirconium compounds, such as a methyl HOSUFINJI cyclopentadienylzirconium dimethyl, Screw (indenyl) titanium diphenyl, a screw (cyclopentadienyl) titanium dialkyl, Screw (cyclopentadienyl) titanium diphenyl, a screw (methylcyclopentadienyl) titanium dialkyl, Screw (1, 2-dimethylcyclopentadienyl) titanium diphenyl, Titanium compounds, such as screw (1, 2-dimethylcyclopentadienyl) titanium dichloride, There are vanadium compounds, such as hafnium compounds, such as screw (cyclopentadienyl) hafnium dichloride and a screw (cyclopentadienyl) hafnium dimethyl, and screw (cyclopentadienyl) vanadium dichloride, etc.

[0024] moreover, as a catalyst by desirable geometric control, concretely -1, 2-ethane diyl zirconium dichloride, (The 3rd class butyl amide) (tetramethyl-eta5-cyclopentadienyl) (3rd class butyl amide)-(tetramethyl-eta5-cyclopentadienyl)-1, 2-ethane diyl titanium dichloride, -1, 2-ethane diyl zirconium dichloride, (Methyl amide) (tetramethyl-eta5-cyclopentadienyl) -1, 2-ethane diyl titanium dichloride, (Methyl amide) (tetramethyl-eta5-cyclopentadienyl) - methylene titanium dichloride, (Ethyl amide) (tetramethyl-eta5-cyclopentadienyl) Dimethyl-(tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, (The 3rd class butyl amide) A dimethyl (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, (The 3rd class butyl amide) (Benzyl amide) There are dimethyl (tetramethyl-eta5-cyclopentadienyl) silane titanium dichloride, a dimethyl (phenyl phosphide) (tetramethyl-eta5-cyclopentadienyl) silane zirconium dibenzyl, etc.

[0025] Moreover, the single site catalyst in this invention can be simultaneously with a co-catalyst. What is indicated by the aforementioned official report can be used about a concrete co-catalyst. They are one or more sorts chosen from organoaluminium compounds, such as an organic aluminum oxy compound which repeats alkyloxy aluminum units, such as methyl aluminoxane and ethyl aluminoxane, and it has as a unit as a desirable co-catalyst, alkylaluminum, and a trialkylaluminium, [Bu₃ NH], [B(C₆H₄ R) 4], C₂B nine H13, water, a Lewis acid, an ammonium salt, etc.

[0026] the alpha olefin system polymerization manufactured using the above-mentioned single site catalyst -- the inside of the body, especially desirable things are one or more sorts of ethylene and the alpha olefin of carbon numbers 3-20 of copolymers The hydroxalkyl machine end concentration which is the (A) component which carried out point ** as this invention constituent can carry out 1-100 weight section combination of the denaturation alpha olefin system polymer which is the aforementioned (B) component to the polyoxymethylene copolymer 100 weight section contained 5xten - five or more mols per one mol of oxy-methylenes. It is the constituent which carried out 5-80 weight section combination of the denaturation alpha olefin system polymer of the (B) component more preferably. (B) If under 1 weight section of the denaturation alpha olefin system polymer

which is a component is inadequate for improvement of tension ductility or a repeat impact strength and it exceeds the 100 weight sections, it will become easy to generate ablation by the light-gage Plastic solid, and tension ductility will also begin to fall.

[0027] Next, the additive which can be added further is stated to the polyoxymethylene copolymer constituent of this invention. If it blends to the total 100 weight section of the above (1) and (2) components in the range of the JI fatty-acid calcium 0.01 which consists of two or more sorts of fatty acids which are carbon numbers 10-36 further - the 0.2 weight sections, the constituent which fits the requirements in this invention further will be obtained. Although either saturated fatty acid, unsaturated fatty acid and the fatty acid replaced by the hydroxyl are good as a fatty acid used for this JI fatty-acid calcium, saturated fatty acid is preferably good. As a fatty acid used, a capric acid, a lauric acid, a tridecyl acid, A myristic acid, pentadecyl acid, a palmitic acid, a heptadecyl acid, stearin acid, A nonadecane acid, arachin acid, behenic acid, a lignoceric acid, a cerotic acid, A montanoic acid, a melissic acid, a cello blastin acid, a undecylenic acid, oleic acid, An elaidic acid, a cetoleic acid, an erucic acid, a brassidic acid, a sorbic acid, Linolic acid, a linolenic acid, an arachidonic acid, a propiolic acid, a steer roll acid, 12-hydroxy dodecanoic acid, a 3-hydroxy decanoic acid, 16-hydroxy hexadecanoic acid, 10-hydroxy hexadecanoic acid, a 12-hydroxy OKUTA decanoic acid, a 10-hydroxy-8-OKUTA decanoic acid, d1-erythro-9, 10-dihydroxy OKUTA decanoic acid, etc. are mentioned. Also in these fatty acids, it is a lauric acid, a tridecyl acid, a myristic acid, pentadecyl acid, a palmitic acid, a heptadecyl acid, stearin acid, a nonadecane acid, arachin acid, and behenic acid preferably, and they are a palmitic acid, a heptadecyl acid, and stearin acid especially preferably.

[0028] Additives other than the above can also be added according to a request. For example, they are inorganic fillers, such as an antioxidant, hindered amine, a polyamide, a melamine, a melamine derivative, the Polly beta alanine copolymer, an ultraviolet ray absorbent, glass fiber, talc, a wollastonite, and a hydrotalcite, conductive carbon black, a pigment, a crystalline-nucleus agent, lubricant, a release agent, an antistatic agent, etc. About especially an antioxidant, it is desirable to add a triethylene-glycol screw [3-(3-t-BUCHIRU 5-MECHIRU 4-hydroxyphenyl) propionate] within the limits of the 0.1 - 1.0 weight section. The polyoxymethylene copolymer constituent of this invention is fabricated by various configurations by the well-known various melting fabricating methods from the former. For example, methods, such as injection molding, extrusion molding, inflation molding, blow molding, compression molding, and foaming, are mentioned, and it is used for large uses including autoparts, an electrical part, information machines and equipment, and industrial miscellaneous goods.

[0029]

[Example] Next, although an example explains this invention in detail, this invention is not limited at all by these examples. First, the parameter and measurement conditions in an example are described.

(1) determination-of-molecular-weight TOSOH CORP. of a polyoxymethylene copolymer and a block copolymer -- HFIP was used as HLC-8120 and HFIP806 (two 30cm columns) by Showa Denko K.K., and a carrier, PMMA by the polymer laboratory company was used as a standard sample, and GPC was measured and calculated by the temperature of 40 degrees C, and flow rate 0.5 ml/min

(2) The number of ends which the polyoxymethylene copolymer, the fixed quantity polyoxymethylene copolymer of the hydroxyalkyl machine of a block copolymer, and the block copolymer were made to react at the temperature below an acetic anhydride and the melting point, acetylated, and was made to acetylate using an infrared absorption spectrum was quantified, and the number of mols per one mol of oxy-methylenes estimated.

[0030] (3) Tension ductility ASTM According to D-638, it measured by 50% of tension speed, and min. In addition, ductility was measured about between 40mm marked lines.

(4) With the repeat impact test vessel made from repeat impact-strength Oriental precision equipment, using the test piece with a notch of 3.2mm thickness, it examined on condition that the frequency for /23 degrees C, 310g load x20mm fall height, and 60 times, and the number of times to destruction was measured. The larger one of a numeric value is repeatedly excellent in a shock fatigue property.

(5) MIASTM According to D-1238, it measured on condition that 190 degrees C and 1m of diameters phi of a cylinder 10mmx die of 2160g [of loads] x.

[0031] (6) The test piece of the configuration shown in hinge property drawing 1 was fabricated, and it evaluated based on the criteria shown below.

measurement size: -- n=10 test method: -- after leaving a sample under -20 degrees C, and 50% environment of RH for 24 hours or more, the hinge region was repeated and bent at the angle of 180 degrees under these conditions

The number which the hinge region destroyed between A:100 evaluation bendings. (The smaller one [numeric value] is excellent.)

What evaluated the hinge region state after performing B:100 evaluation bending by the following criteria, and expressed it with the average mark. (The larger one of a numeric value is excellent.)

5: The thing 1 to which the crack of the thing 3:hinge region front face which the minute crack generated grew up to be the rear face of a thing 4:hinge region at which abnormalities were hardly accepted, the crack of the thing 2:hinge region which became large grew up to be it toward the core further, and the hinge region became very thin : the thing which a break goes into the hinge region which became thin, and it was cutting and of which thing 0:fracture was done [0032] Adjust the paddle type continuation polymerization machine biaxial [with a jacket] which can let a heat carrier pass to 80 degrees C, and the trioxane which is water + formic acid =4ppm (Example 1) By 40 mols / hr 1 and 3-dioxolane is simultaneously supplied to a polymerization machine by two mols / hr as an annular formal. The boron-trifluoride G n-butyl etherate dissolved in the cyclohexane as a polymerization catalyst so that it may become 5xten - five mols to one mol of trioxanes Moreover, as a chain transfer agent, feed of the methanol

was continuously carried out so that it might become 2xten - three mols to one mol of trioxanes, and the polymerization was performed.

[0033] the polymer discharged from the polymerization machine -- triethylamine 1%, after supplying in solution and performing deactivation of a polymerization catalyst completely. The polymer is filtered and washed and the rough polyoxymethylene copolymer 1 weight section after filtration washing is received. as the 4th class ammonium compound It added so that triethyl (2-hydroxyethyl) ammonium formate might be converted into the amount of nitrogen using the aforementioned formula (4) and it might become the 20 weight ppm, and after mixing uniformly, it dried at 120 degrees C.

[0034] Next, to the above-mentioned dryness rough polyoxymethylene copolymer 100 weight section, 0.3 weight section addition of the triethylene-glycol screw [3-(3-t-BUCHIRU 5-MECHIRU 4-hydroxyphenyl) propionate] was carried out as an antioxidant, and the biaxial [with a vent] screw-type extruder was supplied. Water and/or the triethylamine were added if needed to the polyoxymethylene copolymer which is fusing in an extruder, and the unstable end was decomposed in residence-time 5 minutes in the setting temperature of 200 degrees C of an extruder, and an extruder. The polyoxymethylene copolymer into which the unstable end was decomposed was devolatilized under the condition of vent degree of vacuum 20Torr, and from the extruder dice section, it was extruded as a strand and it pelletized it (polyoxymethylene copolymer P-**).

[0035] In this way, a part of obtained polyoxymethylene copolymer P-** was taken out, and the fixed quantity of the determination of molecular weight by GPC and an end hydroxyalkyl machine was performed. Nylon 66 ground by the maleic-anhydride graft denaturation ethylene butene-1 copolymer (density 0.89 g/cm³, 15% of degree of crystallinity) 25 weight section and 4micro of mean particle diameters which furthermore carried out maleic-anhydride 0.9 weight section graft copolymerization to the 100 weight sections of polyoxymethylene copolymer P-** was supplied to the account of back to front biaxial extruder which added, respectively and mixed the 0.05 weight section uniformly, melting kneading was carried out again, and the pellet was obtained. The physical-properties test piece was created using Sumitomo injection-molding-machine SH-75 which set this pellet as 200 degrees C of cylinder temperatures, and 70 degrees C of die temperatures after 24-hour dryness at 80 degrees C, and physical-properties evaluation was performed. The result was shown in Table 2-1.

[0036] (Example 2) In the example 1, except having used further 1xten - three mols [(CH₃O)₂CH₂] of 1xten - three mols of methylals for the methanol to one mol of trioxanes to one mol of trioxanes as a chain transfer agent, the same operation as an example 1 was performed, and physical-properties evaluation was carried out. The result is shown in Table 2-1.

(Example 3) In the example 1, except having used further 0.25xten - three mols [(CH₃O)₂CH₂] of 1.75xten - three mols of methylals for the methanol to one mol of trioxanes to one mol of trioxanes as a chain transfer agent, the same operation as an example 1 was performed, and physical-properties evaluation was carried out.

[0037] The result is shown in Table 2-1.

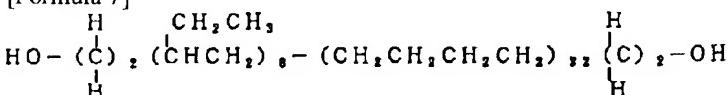
The trioxane which is 4 ppm Water + formic acid = (Examples 4-7) By 40 mols / hr 1 and 3-dioxolane is simultaneously supplied to a polymerization machine by two mols / hr as an annular formal. The boron-trifluoride G n-butyl etherate dissolved in the cyclohexane as a polymerization catalyst so that it may become 10xten - five mols to one mol of trioxanes Moreover, as a chain transfer agent, feed of the both-ends hydroxyl polyethylene (Mn=5000) was continuously carried out so that it might become 0.5xten - three mols to one mol of trioxanes, and the polymerization was performed. Except the above, the same operation as an example 1 was performed, and the polyoxymethylene copolymer Q was obtained. A part of obtained polyoxymethylene copolymer Q was taken out, and the fixed quantity of the determination of molecular weight by GPC and an end hydroxyalkyl machine was performed.

[0038] Furthermore, the denaturation alpha olefin system copolymer 25 weight section was blended with the polyoxymethylene copolymer Q100 weight section by composition of Table 1-1 - 1-2, and also the monochrome palmitic-acid-monostearin acid calcium 0.04 weight section was added, melting kneading was carried out again, and the pellet was obtained. This pellet performed physical-properties evaluation like the example 1. This result is shown in Table 2-1 - 2-2.

[0039] The trioxane which is 4 ppm Water + formic acid = (Examples 8-12) By 40 mols / hr 1 and 3-dioxolane is simultaneously supplied to a polymerization machine by one mol / hr as an annular formal. The boron-trifluoride G n-butyl etherate dissolved in the cyclohexane as a polymerization catalyst so that it may become 10xten - five mols to one mol of trioxanes Moreover, as a chain transfer agent, feed of the both-ends hydroxyl hydrogenation polybutadiene (Mn=2330) of the following formula (5) was continuously carried out so that it might become 1xten - three mols to one mol of trioxanes, and the polymerization was performed. Except the above, the same operation as an example 1 was performed, and the polyoxymethylene copolymer R was obtained.

[0040]

[Formula 7]



• • • (5)

In this way, a part of obtained polyoxymethylene copolymer R was taken out, and the fixed quantity of the determination of molecular weight by GPC and an end hydroxyalkyl machine was performed.

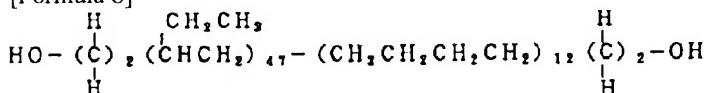
[0041] On the other hand, (3rd class butyl amide)-(tetramethyl-eta5-cyclopentadienyl)-1 and 2-ethane diyl titanium dichloride is

used as a catalyst. Maleic-anhydride graft denaturation ethylene octene 1 copolymer 25 which carried out maleic-anhydride 0.9 weight section graft copolymerization to ethylene octene 1 copolymer of the Table 1-2 - 1-3 which manufactured by the method given in JP,3-163088,A - 40 weight sections In the polyoxymethylene copolymer R100 weight section, it added with the monochrome palmitic-acid-monostearin acid calcium 0.04 weight section, melting kneading was carried out again, and the pellet was obtained. This pellet performed physical-properties evaluation like the example 1. This result is shown in Table 2-2 - 2-3.

[0042] The trioxane which is 4 ppm Water + formic acid = (Examples 13-17) By 40 mols / hr 1 and 3-dioxolane is simultaneously supplied to a polymerization machine by two mols / hr as an annular formal. The boron-trifluoride G n-butyl etherate dissolved in the cyclohexane as a polymerization catalyst so that it may become 10xten - five mols to one mol of trioxanes Moreover, feed was carried out continuously and the polymerization was performed so that it might become the rate which shows the both-ends hydroxyl hydrogenation polybutadiene ($M_n=3390$) of the following formula (6) in Table 1-3 - 1-4 to one mol of trioxanes as a chain transfer agent. Except the above, the same operation as an example 1 was performed, and polyoxymethylene copolymer S** - ** were obtained.

[0043]

[Formula 8]



. . . (6)

In this way, a part of obtained polyoxymethylene copolymer S** - ** were taken out, and the fixed quantity of the determination of molecular weight by GPC and an end hydroxyalkyl machine was performed. On the other hand, (3rd class butyl amide)-(tetramethyl-eta5-cyclopentadienyl)-1 and 2-ethane diyl titanium dichloride is used as a catalyst. Maleic-anhydride graft denaturation ethylene octene 1 copolymer 20 which carried out maleic-anhydride 0.9 weight section graft copolymerization to ethylene octene 1 copolymer of the Table 1-3 - 1-4 which manufactured by the method given in JP,3-163088,A - 60 weight sections According to composition of Table 1, in polyoxymethylene copolymer S** - **100 weight section, it added with the monochrome palmitic-acid-monostearin acid calcium 0.04 weight section, melting kneading was carried out again, and the pellet was obtained. This pellet performed physical-properties evaluation like the example 1. This result is shown in Table 2-3 - 2-4.

[0044] (Example 1 of comparison) The polyoxymethylene copolymer Q independent physical properties used in the examples 4-7 were evaluated, and it was shown in Table 2-5.

(Example 2 of comparison) Except having added the 0.05 weight section, respectively, having mixed uniformly, and having carried out melting kneading of Nylon 66 ground by the maleic-anhydride graft denaturation ethylene butene-1 copolymer (density 0.89 g/cm³, 15% of degree of crystallinity) 200 weight section and 4micro of mean particle diameters which carried out maleic-anhydride 0.9 weight section graft copolymerization to the polyoxymethylene copolymer Q100 weight section again, the same operation as an example 1 was performed, and physical properties were evaluated. This result is shown in Table 2-5.

[0045] (Examples 3-7 of comparison) Except having used the methylal [(CH₃O)₂CH₂] for the chain transfer agent, the completely same operation as an example 1 was performed, and the polyoxymethylene copolymer T was obtained. A part of obtained polyoxymethylene copolymer T** - ** were taken out, and the fixed quantity of the determination of molecular weight by GPC and an end hydroxyalkyl machine was performed. Moreover, Nylon 66 ground by polyoxymethylene copolymer T** - **100 weight section at the alpha olefin copolymer or the denaturation alpha olefin copolymer 25 - 40 weight sections, and 4micro of mean particle diameters of Table 1-5 was supplied to the account of back to front biaxial extruder which added, respectively and mixed the 0.05 weight section uniformly, melting kneading was carried out again, and the pellet was obtained. This pellet performed physical-properties evaluation like the example 1. This result is shown in Table 2-5 - 2-6.

[0046] (Example 18) In the polyoxymethylene copolymer S-**75 weight section and the polyoxymethylene copolymer T-**25 weight section (3rd class butyl amide)-(tetramethyl-eta5-cyclopentadienyl)-1 and 2-ethane diyl titanium dichloride is used as a catalyst. To ethylene octene 1 copolymer manufactured by the method given in JP,3-163088,A The maleic-anhydride graft denaturation ethylene octene 1 copolymer (30% [of octene content], MI=10) 25 weight section which carried out maleic-anhydride 0.9 weight section graft copolymerization, The calcium-stearate 0.02 weight section and the behenic acid calcium 0.02 weight section were added, melting kneading was carried out again, and the pellet was obtained. This pellet performed physical-properties evaluation like the example 1. This result is shown in Table 2-4.

[0047] (Example 19) Except having considered as the polyoxymethylene copolymer S-**50 weight section and the polyoxymethylene copolymer T-**50 weight section, the same operation as an example 18 was performed, and physical-properties evaluation was performed. This result is shown in Table 2-4.

(Example 20) Except having considered as the polyoxymethylene copolymer S-**25 weight section and the polyoxymethylene copolymer T-**75 weight section, the same operation as an example 18 was performed, and physical-properties evaluation was performed. This result is shown in Table 2-4.

[0048]

[Table 1]

表 1 - 1

		実施例 1	実施例 2	実施例 3	実施例 4	実施例 5
ポリ	トリオキサン(mM/hr)	40	40	40	40	40
オキ	1,3-ジオキサン(mM/hr)	2	2	2	2	2
シメ	連鎖移動剤①(種類)	メノール	メノール	メノール	HO-PE ²⁾	HO-PE ²⁾
チレ	連鎖移動剤②(種類)		メタノール	メタノール		
ン共	連鎖移動剤①(mM/hr)	0.08	0.04	0.01	0.02	0.02
重合	連鎖移動剤②(mM/hr)		0.04	0.07		
体	G P C (Mn)	65000	66000	65000	120000	120000
	オキシメチレン 1 モル当たりのヒドロキシアル基のモル数	6.7×10^{-4}	3.3×10^{-4}	0.8×10^{-4}	3.3×10^{-4}	3.3×10^{-4}
	ポリオキシメチレン共重合体	P-①	P-②	P-③	Q	Q
変性	α-オレフィン①種類	エチレン	エチレン	エチレン	エチレン	エチレン
α-	α-オレフィン②種類	ブテン-1	ブテン-1	ブテン-1	ブテン-1	オクテノ-1
オレ	α-オレフィン①(モル%)	80	80	80	80	80
フィ	α-オレフィン②(モル%)	20	20	20	20	20
ン系	変性剤種類	MAH ¹⁾				
重合	変性剤(g/100g基剤)	0.9	0.9	0.9	0.9	0.9
体	M I (g/10min)	1	1	1	1	10

1) 無水マレイン酸

2) 両末端ヒドロキシル基ポリエチレン (Mn = 5000)

[0049]

[Table 2]

表 1 - 2

		実施例 6	実施例 7	実施例 8	実施例 9	実施例 10
ポリ	トリオキサン(mM/hr)	40	40	40	40	40
オキ	1,3-ジオキサン(mM/hr)	2	2	1	1	1
シメ	連鎖移動剤(種類)	HO-PE ²⁾	HO-PE ²⁾	HO-BD ⁴⁾	HO-BD ⁴⁾	HO-BD ⁴⁾
チレ	連鎖移動剤(mM/hr)	0.02	0.02	0.04	0.04	0.04
ン共	G P C (Mn)	120000	120000	62000	62000	62000
重合	オキシメチレン 1 モル当たりのヒドロキシアル基のモル数	3.3×10^{-4}	3.3×10^{-4}	6.6×10^{-4}	6.6×10^{-4}	6.6×10^{-4}
体	ポリオキシメチレン共重合体	Q	Q	R	R	R
変性	α-オレフィン①種類	エチレン	エチレン	エチレン	エチレン	エチレン
α-	α-オレフィン②種類	オクテノ-1	ブチルベン	オクテノ-1	オクテノ-1	オクテノ-1
オレ	α-オレフィン①(モル%)	80	80	90	80	70
フィ	α-オレフィン②(モル%)	20	20	10	20	30
ン系	変性剤種類	NAH ³⁾	MAH ¹⁾	MAH ¹⁾	MAH ¹⁾	MAH ¹⁾
重合	変性剤(g/100g基剤)	0.9	0.9	0.9	0.9	0.9
体	M I (g/10min)	8	1	1	1	1

1) 無水マレイン酸

2) 両末端ヒドロキシル基ポリエチレン (Mn = 5000)

3) 無水ナジツク酸

4) 両末端ヒドロキシル基水素添加ポリブタジエン (Mn = 2330)

[0050]

[Table 3]

表 1 - 3

		実施例11	実施例12	実施例13	実施例14	実施例15
ボリ	トリオキサン(mol/hr)	40	40	40	40	40
オキ	1,3-ジオキサン (mol/hr)	1	1	2	2	2
シメ	連鎖移動剤①(種類)	HO-BD ⁴⁾	HO-BD ⁴⁾	HO-BD ⁵⁾	HO-BD ⁵⁾	HO-BD ⁵⁾
チレ	連鎖移動剤②(種類)			メラ・ル	メラ・ル	
ン共	連鎖移動剤①(mol/hr)	0.04	0.04	0.04	0.06	0.08
重合	連鎖移動剤②(mol/hr)			0.04	0.02	
体	G P C (Mn)	62000	62000	54000	56000	57000
	オキシメチレン1モル当たりのヒドロキシアル基のモル数	6.6×10^{-4}	6.6×10^{-4}	6.7×10^{-4}	9.9×10^{-4}	13.3×10^{-4}
	ポリオキシメチレン共重合体	R	R	S-①	S-②	S-③
変性	α -オレフイン①種類	イチレン	イチレン	イチレン	イチレン	イチレン
α -	α -オレフイン②種類	カテン-1	カテン-1	カテン-1	カテン-1	カテン-1
オレ	α -オレフイン①(モル%)	70	70	80	70	70
フィ	α -オレフイン②(モル%)	30	30	20	30	30
ン系	変性剤種類	MAH ¹⁾				
重合	変性剤(g/100g基剤)	0.9	0.9	0.9	0.9	0.9
体	M I (g/10min)	10	10	1	10	10

1) 無水マレイン酸

4) 両末端ヒドロキシル基水素添加ポリブタジエン (Mn = 2330)

5) 両末端ヒドロキシル基水素添加ポリブタジエン (Mn = 3390)

[0051]

[Table 4]

表 1 - 4

		実施例16	実施例17
ボリ	トリオキサン(mol/hr)	40	40
オキ	1,3-ジオキサン (mol/hr)	2	2
シメ	連鎖移動剤①(種類)	HO-BD ⁵⁾	HO-BD ⁵⁾
チレ	連鎖移動剤②(種類)		
ン共	連鎖移動剤①(mol/hr)	0.08	0.08
重合	連鎖移動剤②(mol/hr)		
体	G P C (Mn)	57000	57000
	オキシメチレン1モル当たりのヒドロキシアル基のモル数	13.3×10^{-4}	13.3×10^{-4}
	ポリオキシメチレン共重合体	S-③	S-③
変性	α -オレフイン①種類	イチレン	イチレン
α -	α -オレフイン②種類	カテン-1	カテン-1
オレ	α -オレフイン①(モル%)	70	70
フィ	α -オレフイン②(モル%)	30	30
ン系	変性剤種類	MAH ¹⁾	MAH ¹⁾
重合	変性剤(g/100g基剤)	0.9	0.9
体	M I (g/10min)	10	10

1) 無水マレイン酸

5) 両末端ヒドロキシル基水素添加ポリブタジエン (Mn = 3390)

[0052]

[Table 5]
表 1-5

		比較例3	比較例4	比較例5	比較例6	比較例7
ボリ	トリオキサン(mL/hr)	40	40	40	40	40
オキ	1,3-ジオキサン(mL/hr)	2	2	2	2	2
シメ	連鎖移動剤(種類)	メチル	メチル	メチル	メチル	メチル
チレ	連鎖移動剤(mL/hr)	0.08	0.08	0.08	0.08	0.04
ン共	G P C (Mn)	52000	62000	52000	52000	98000
重合	オキシメチレン1モル当たりの ヒドロキシアル基のモル数	1.3×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	1.3×10^{-5}	1.2×10^{-5}
体	ポリオキシメチレン共重合体	T-①	T-①	T-①	T-①	T-②
変性	α -オレフィン①種類	イチレン	イチレン	イチレン	イチレン	イチレン
α -一	α -オレフィン②種類	ブテン-1	オクテン-1	ブチル	オクテン-1	オクテン-1
オレ	α -オレフィン①(モル%)	80	80	80	80	80
フィ	α -オレフィン②(モル%)	20	20	20	20	20
ン系	変性剤種類				MAH ¹⁾	MAH ¹⁾
重合	変性剤(g/100g基剤)				0.9	0.9
体	M I (g/10min)	1	1	1	1	1

1) 無水マレイン酸

[0053]

[Table 6]
表 2-1

		実施例1	実施例2	実施例3	実施例4	実施例5
ボリ	種類①	P-①	P-②	P-③	Q	Q
シメ	種類②					
ン共	種類①(重量部)	100	100	100	100	100
重合	種類②(重量部)					
体						
変性	基剤種類	イチレン-ブテン-1	イチレン-ブテン-1	イチレン-ブテン-1	イチレン-ブテン-1	イチレン-オクテン-1
α -一						
オレ	変性剤種類	MAH	MAH	MAH	MAH	MAH
フィ	変性 α -オレフィン重合体(25	25	25	25	25
ン系	重量部)					
重合						
度	M I (g/10min)	14.2	13.8	13.9	1.8	1.7
溶融	引張り伸度(%)	108	106	75.5	142	145
混練	繰り返し衝撃強度(回)	10800	10500	6800	11000	11100
後の	ヒンジ特性					
物性	A評価	0	0	0	0	0
評価	B評価	4.2	4.1	3.4	4.0	4.1

1) 無水マレイン酸

[0054]

[Table 7]

表 2-2

		実施例 6	実施例 7	実施例 8	実施例 9	実施例 10
ポリオ キシカ ン共 重合 体	種類① 種類② 種類① (重量部) 種類② (重量部)	Q 100	Q 100	R 100	R 100	R 100
変性 α- オレフィ ン系 重合 体	基剤種類 変性剤種類 変性 α-オレフィン重合体 (重量部)	イチレン-オクテン - 1 NAH 25	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 25
再度 溶融 混練 後の 物性 評価	M I (g/10min) 引張り伸度(%) 繰り返し衝撃強度(回) ヒンジ特性 A評価 B評価	1.8 108 10100 0 4.1	1.9 148 10800 0 4.3	11.3 151 15200 0 4.6	10.9 155 16000 0 4.7	11.0 156 15900 0 4.8

[0055]

[Table 8]

		実施例 11	実施例 12	実施例 13	実施例 14	実施例 15
ポリオ キシカ ン共 重合 体	種類① 種類② 種類① (重量部) 種類② (重量部)	R 100	R 100	S 100	S 100	S 100
変性 α- オレフィ ン系 重合 体	基剤種類 変性 α-オレフィン重合体 (重量部)	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 40	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 25	イチレン-オクテン - 1 MAH 20
再度 溶融 混練 後の 物性 評価	M I (g/10min) 引張り伸度(%) 繰り返し衝撃強度(回) ヒンジ特性 A評価 B評価	13.7 158 15500 0 4.7	4.4 154 16800 0 4.6	11.1 152 15500 0 4.7	11.4 157 16800 0 4.8	12.2 145 14900 0 4.6

表 2-3

[0056]
[Table 9]

		実施例16	S	実施例17	S	実施例18	S-③ T-①	実施例19	S-③ T-①	実施例20
ガリブ キシ好 レジ共 重合 体	種類① 種類② 種類① (重量部) 種類② (重量部)	100	100	75	75	50	50	50	25	S-③ T-①
基性 α - カーフィ ン系 重合 体	イチジンカーテン - 1 イチジンカーテン - 1			イチジンカーテン - 1	75					
再度 溶融 混練 後の 物性 評価	M.I (g/10min) 引張り伸長(%) 繰り返し衝撃強度(回) ヒンジ特性	MAH 40	MAH 60	MAH 25	MAH 25	MAH 16200	MAH 15200	MAH 15600	MAH 12100	MAH 12900
A評価 B評価				0 4.9	0 4.9	0 4.7	0 4.8	0 4.8	0 4.6	

表 2-4

[0057]
[Table 10]

	比較例 1 Q	比較例 2 Q	比較例 3 T-①	比較例 4 T-②	比較例 5 T-③
(重量部) (重量部)	100	100	100	100	100
類 種類 一オルガン重合体 部)	MAH 200	MAH 25	MAH 25	MAH 25	MAH 25
'10min) 伸度(%) し衝撃強度(回) 特性	23.3 39 2300 10 0	0.9 150 19000 7 1.7	13.3 14 1700 10 0.2	12.9 10 1600 10 0	13.0 16 1600 10 0.4

[0058]

[Table 11]
表 2-6

		比較例 6	比較例 7
ポリオ キシケ ン共 重合 体	種類① 種類② 種類①(重量部) 種類②(重量部)	T-① 100	T-② 100
変性 α - オレフィ ン系 重合 体	基剤種類 変性剤種類 変性 α -オレフィン重合体 (重量部)	イソブレン-オクテン-1 MAH 25	イソブレン-オクテン-1 MAH 40
再度 溶融 混練 後の 物性 評価	M I (g/10min) 引張り伸度(%) 繰り返し衝撃強度(回) ヒンジ特性 A評価 B評価	13.5 44 2900 5 1.2	4.4 27 2400 10 0.8

[0059]

[Effect of the Invention] the constituent of the polyoxymethylene copolymer and/or the polyoxymethylene block copolymer which has the hydroxyalkyl machine molecule end of this invention, and a specific denaturation alpha olefin system polymer -- 1. -- high tension ductility and 2. -- the material of fields, such as the high repeat impact strength, the field which make satisfy three simultaneously and 3. needs flexibility and shock-resistant fatigue strength using the resin constituent especially the autoparts, the electrical part, the information machines and equipment, the industrial miscellaneous goods, etc. of the outstanding low-temperature hinge property, was able to offer

[Translation done.]